BIOPETROL SYNTHESIZED FROM RUBBER SEED OIL BY ZEOLITES CATALYST : EFFECT OF OPERATING TEMPERATURE IN CRACKING PROCESS

MOHD AZWAN BIN MOHD SADERI

Report submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

Petroleum is a fossil fuel which takes millions of years to form. The fossil fuel that used today depleting much faster without suspected. The alternatives fuel must be searched to solve this problems. The rubber seed oil is found to be a promising alternative fuel source to replace petrol fuel. Biopetrol is derived from vegetable oil and also renewable energy source. The objectives of this research are to synthesize biopetrol from rubber seed oil in order to overcome fuel supply problem and to identify the effect of temperature in cracking process using zeolites catalyst for the rubber seed oil production. Soxhlet extractor is used to extract the rubber seed oil from the rubber seed. Then, the hexane is removed by using rotary evaporator to get pure rubber seed oil. The catalytic cracking with presence zeolites as the catalyst is applied to crack the fatty acid complex into smaller hydrocarbon molecules. Five grams of zeolites catalyst is added into the crucible that contain 25 ml rubber seed oil. The mixture is heated in the furnace at 300°C for 15 minutes. After that, the different temperature is used which is 350°C and 400°C in order to see the effect of temperature on the isooctane production. By using the gas chromatography, the presence of isooctane in the sample can be detected which is indicate that biopetrol is produced. Based on this research, the highest amount of isooctane is produced which is 75.3234% at temperature of 350ºC. The presence of temperature and catalyst that used will give the sudden effect to production of isooctane from the rubber seed oil. In conclusion, biopetrol can be produced from the rubber seed oil by zeolites catalyst.

ABSTRAK

Petroleum adalah bahan api fosil yang mengambil masa berjuta-juta tahun untuk terbentuk. Bahan api fosil yang digunakan hari ini semakin berkurangan dengan lebih cepat tanpa disedari. Bahan api alternatif perlu dicari untuk menyelesaikan masalah ini. Minyak biji getah (RSO) didapati menjadi sumber bahan api alternatif yang menjanjikan untuk menggantikan bahan api petrol. Biopetrol berasal daripada minyak sayur-sayuran dan juga sumber tenaga yang boleh diperbaharui. Objektif penyelidikan ini adalah untuk mensintesis biopetrol daripada RSO untuk mengatasi masalah bekalan bahan api dan untuk mengenal pasti kesan suhu dalam proses retak dengan menggunakan pemangkin zeolite untuk pengeluaran minyak biji getah. Alat soxhlet ekstrak digunakan untuk mengekstrak RSO dari bijinya. Kemudian, heksana dikeluarkan dengan menggunakan penyejat putar untuk mendapatkan RSO tulen. Proses retak dengan kehadiran zeolite sebagai pemangkin digunakan untuk memecahkan asid lemak kompleks kepada molekul hidrokarbon yang lebih kecil. Lima gram pemangkin zeolite dituang ke dalam mangkuk pijar yang mengandungi 25 ml RSO. Campuran dipanaskan di dalam ketuhar pada suhu 300ºC selama 15 minit. Selepas itu, suhu yang berbeza iaitu 350ºC dan 400ºC digunakan untuk melihat kesan suhu ke atas pengeluaran isooktana. Dengan menggunakan alat gas kromatografi, kehadiran isooktana dalam sampel boleh dikesan yang menunjukkan juga bahawa biopetrol dihasilkan. Berdasarkan kajian ini, jumlah tertinggi isooktana adalah 75.3234% iaitu pada suhu 350ºC. Kehadiran suhu dan pemangkin yang digunakan telah memberi kesan kepada pengeluaran isooktana daripada RSO. Kesimpulannya, biopetrol boleh dihasilkan daripada RSO dengan menggunakan pemangkin zeolite.

TABLE OF CONTENTS

CHAPTER 5 CONCLUSION AND RECOMMENDATION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

O_2	Oxygen
CO_2	Carbon Dioxide
H_2	Hydrogen
N_2	Nitrogen
°F	Fahrenheit
%	Percentage
°C	Celsius
g	gram
ml	millilitre
µl	microlitre
m	meter
mm	millimetre
min	minutes
pA*s	peak area
kPa	kilo paschal

LIST OF ABBREVIATIONS

CI	Compression ignition
GRG	General rubber goods
HCCI	Homogeneous charge compression ignition
PRF	Primary reference fuel
SI	Spark ignition
RSO	Rubber seed oil
LPG	Liquefied petroleum gas
GC	Gas chromatography
GLC	Gas liquid chromatography
GSC	Gas solid chromatography
WCOT	Wall-coated open tubular
SCOT	Support-coated open tubular
CEC	Cation exchange capacity
GCMS	Gas chromatography mass spectrometry

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Petrol or gasoline is a complex mixture of over 500 hydrocarbons that may have between 5 to 12 carbons. It is produced by mixing fractions obtained from the distillation of crude oil (petrochemicals) with brand-specific additives to improve performance. It is a volatile liquid with a characteristic odour under normal conditions. In this century, petrol is the most demanding fuel. Usually, petrol is mainly used as a fuel for road vehicles such as cars, motorbikes and vans. In smaller engines (two stroke), petrol is mixed with oil to produce a fuel mixture that can reduces engine wear. However, petrol is non-renewable energy.

The solution of petrol demand is biofuel. Biofuel can be defined as combustible plant or animal material that can be used as an energy source. The simplest example of biofuel is wood. Wood-burning as a heat and light source has been popular for millennia. Biofuels are also made from sugar cane, soybean algae, vegetable oil and others. The environmental pollution and diminishing supply of the fossil fuels in today are the main factor leading to search for finding the alternative source of energy. When the petrol or diesel are burnt, the carbon atoms will react with O_2 at atmosphere to form Carbon Dioxide (CO_2). This situation can contribute to global warming and also greenhouse effect. Biofuel or bioorganic fuel is considered to be more environmentally responsible type of fuel compared to original oil and fossil fuel product. They have many advantages in terms of ecological sustainability.

Biopetrol or the alternative for petrol is derived from vegetable oil and it is renewable energy sources. The characteristics of biopetrol are it is no sulphur content, non toxic, offer no storage difficulty and excellent lubrication properties. It is proven by many research has been done before. Many developing and industrialized country such as Japan have expressed interest to this relevant idea.

The rubber seed oil, a non-edible type of vegetable oil has been considered as a potential alternative fuel for compression ignition (ci) engines. It has contain many fatty acid in order to produce biopetrol. In this research, catalytic cracking with presence of zeolites catalyst is applied to break the fatty acid in the rubber seed oil to get the isooctane.

1.2 PROBLEM STATEMENT

Petroleum is formed from the remains of tiny sea plants and animals that died millions of years ago. It is a non renewable energy source. This petroleum source cannot be depended at all because petroleum will be exhausted. Oil is the limited resource and has high demands every time. In the middle of 2008, the oil price increase dramatically as shown in Figure 1.1 and Figure 1.2. The instability of the oil world, give the bad response to the peoples in the world. It is because everything to be more expensive caused by the increasing price of petrol. Thus, the alternative source for petroleum is important in overcome this problem. The alternative source like biopetrol is the answer for this polemic because it is cheaper and safer than fossil fuel.

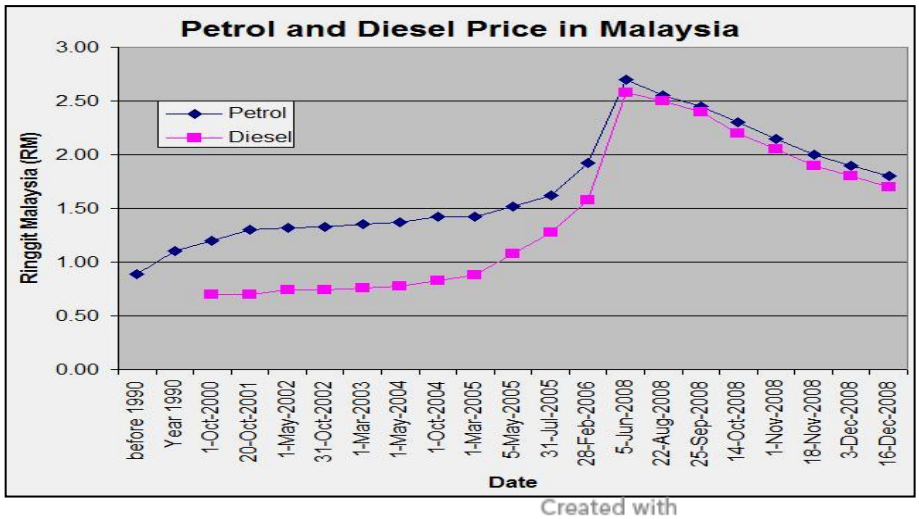

Figure 1.1 : Complete Malaysia Petrol and Diesel Price Chart Since 1990 (updated 0n Jan 09)

Source: OPEC (2008)

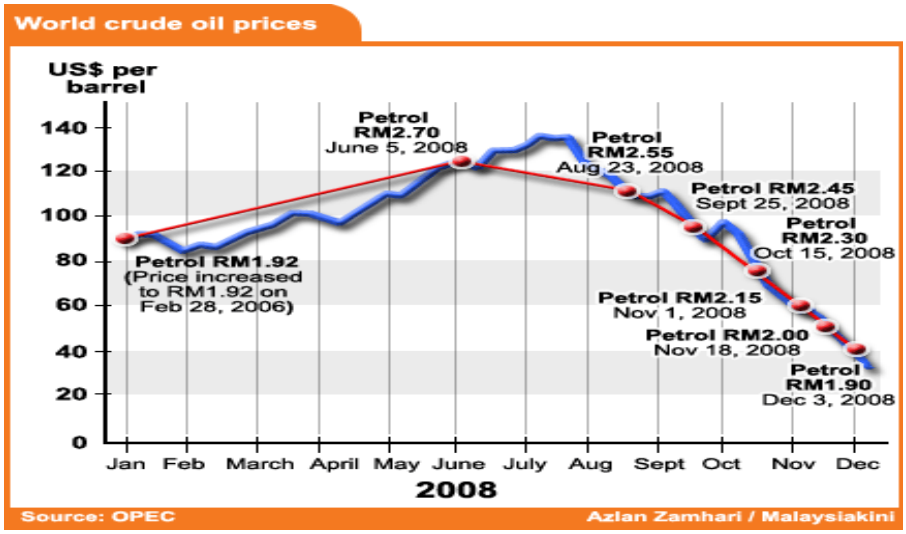

Figure 1.2 : World Crude Oil Prices

Source: OPEC (2008)

Petroleum fuels which is used for power vehicles, household heat generation, generate electric power are the main causes of air pollution. The use of petroleum every day can give the bad effect to environment. When the petroleum is burning, it will generates gases such as carbon monoxide, nitrogen oxides and sulphur dioxides. Sulphur dioxide and nitrogen oxides can react with water in the atmosphere. This situation can increase the acidity of water. Then, the water fall back to the surface earth and damaging property and pollute the environment. This phenomenon is called acid rain.

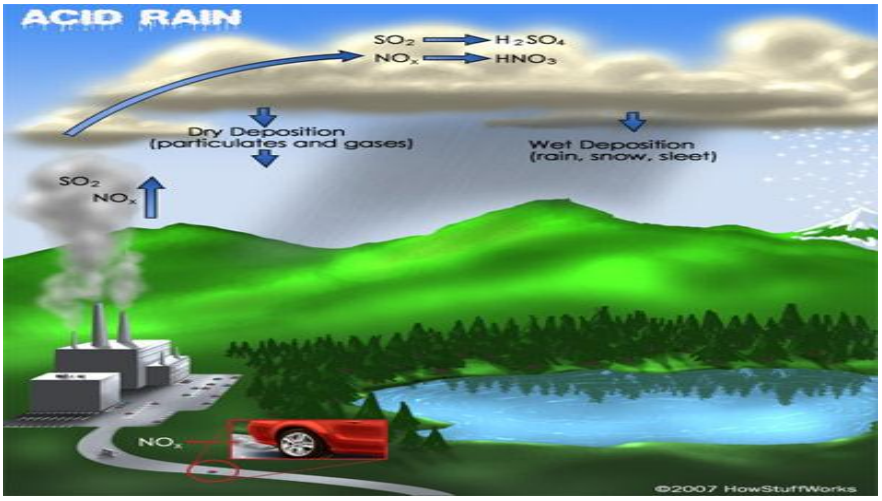

Figure 1.3 : Acid Rain Production

Source : Ramadhas A.S. et al. (2005)

Besides, some of scientist believes that petroleum use is the cause in global climate change. As a result, the average temperature of Earth's surface increases from 0.7 to 1.4°F since the late 1800's. The raising concentrations of green house gases also are responsible for some or all this warming. Carbon dioxide and methane are the gas from greenhouse will trap heat from the sun and hold it near Earth's surface. After the beginning of Industrial Revolution from the late 1700's to the mid-1800's, the concentration of carbon dioxide increase by 30 percent. On the that time, large amounts of petroleum and coal are used by people as power-driven machinery largely replaced hand labour. Some scientist who believes human activities contribute to global warming are concerned that warming in the earth will continue and accelerate if fossil fuel consumption continues to grow.

Malaysia is the third largest rubber producer in the world. In 1980, Malaysia has 2.0 million hectare of rubber plantation, however it declined to 1.2 million hectare in 2007. Although, the supply rubber wood declining, value added rubber wood products still continues to be a major export. The use of rubber is widespread, ranging from industrial product and household, entering the production stream at the intermediate stage or as final products. Usually, tire and tube are the largest consumers of rubber. For remaining which is 44% are taken up by the general rubber goods (GRG) sector, which

includes all products except tires and tubes. Even the rubber seeds from the rubber plant are not utilized like latex. Actually, rubber seed have many fatty acids which can produce oil. Rubber seed oil can be used in biopetrol production. Biopetrol from the rubber seed oil is comparable with petrol in the market. Even, it has many advantages than petrol. Rubber seed use should be explored and commercialized because it can prevent fuel problem in the future.

Figure 1.4 : Rubber Seed

Source: Ramadhas A. S. et al. (2005)

Fossil fuel take millions years to produce. It was formed from dead plants and animals. The fossil fuel that used today depleting much faster without suspected. Many industries use large amount of fossil fuels to power their machines. The industries which are contributed to the depletion of fossil fuels are the automotive industries, metal industries and also transportation. Besides, individual citizens also to be the factor of depletion of fossil fuel where they the use of electricity and driving cars as example everyday.

The challenge of synthesizing biogasoline from vegetable oils, for example rubber seed oil in this research is the competition of bioalcohols (biomethanol and bioethanol), hydrogen and water those also synthesized for gasoline-used vehicles. Bioalcohols are currently used by several types of latest generation vehicles as alternative of gasoline, however only low portions of bioalcohols are applicable in their mixtures with gasoline, for example 5%, 10% and 25% bioalcohols in E05, E10 and E25 blends without any modifications of gasoline-used engine. This is because bioalcohols are miscible and

soluble with water those give negative effect to the engine itself, especially rust and corrosion, even their octane numbers are higher (112 for bioethanol and 106 for biomethanol). Those negative effects possibly occur when the high concentrations of bioalcohols are applied, for example 85% bioalcohol in E85 blend. In order to prevent the negative effect occurrences, the engine should be modified.

1.3 RESEARCH OBJECTIVES

i. To synthesize biopetrol from rubber seed oil in order to overcome fuel supply problem.

ii. To identify the effect of temperature in cracking process using zeolites catalyst for the rubber seed oil production.

1.4 SCOPES OF RESEARCH

In order to achieve the research objectives, the scopes have been identified. There are some scopes that must to be focus in this research:

i. The extraction of rubber seed oil from rubber seeds using Soxhlet Extraction.

ii. The cracking process to crack the fatty acid complex into smaller hydrocarbon molecules.

iii. Using the gas chromatography method to determine the concentration of Isooctane.

1.5 RATIONALE AND SIGNIFICANCE

i. Biopetrol is a renewable energy source and is biodegradable.

ii. Biopetrol helps to reduce pollution and prevent the greenhouse effect

iii. Fatty acid can be found easily in most vegetable oil especially in rubber seed oil

iv. Rubber seeds are easy to be found in Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 PETROLEUM

Petroleum is a fossil fuel. It was formed from remains of animals and tiny sea plants that died millions of years ago. The animals and plants which were died would sink to the bottom of the oceans. Then, they were buried by thousands of feet of sediment and sand that turned into rock. Over time, this organic mixture was subjected to enormous pressure and heat as the layers are increased. The mixture changed chemically, breaking down into compounds made of hydrogen and carbons atoms. This formation can only take place within certain geological conditions. Only 2 % of the organic material is transformed into oil under this condition. The crude oil is pumped out of the ground in a black thick liquid solution is also known as petroleum. Petroleum is non-renewable energy source. It cannot form in the short time. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO_2 (Shay, 1993).

2.2 ISOOCTANE

Isooctane or the other name 2,2,4-Trimethylpentane is an octane isomer which defines the 100 point on the octane rating scale. In gasoline, isooctane is the important component for it. Usually, the production of isooctane in the petroleum industries is in the big scale because the many application of it in this century. In the alkylation's process, isobutane react with isobutylene by using a strong acid catalyst. Isobutylene is demerized into isooctane and after that, it is hydrogenated to isooctane in the nexoctane. The best properties of isooctane is it has low toxicity, high colour stability, lack of

colour, low odour and rapid evaporation which makes it an excellent solvent for a variety of surface applications.

There are a lot of interest using isooctane as a fuel in investigations of homogeneous charge compression ignition engine (HCCI) in which isooctane is used both as a neat fuel and also as a component in a primary reference fuel blend. Isooctane can improve the efficiency and also performance of currently operating combustors. Besides, it can reduce the production of pollutant species emissions generated in the combustion process. Isooctane is a primary reference fuel (PRF) for octane rating in spark-ignition engine, and when used in compression ignition engine, has a cetane number of approximately 15 (Curran H.J. et al., 2002)

Table 2.1 : Properties of Isooctane

Physical & Chemical Properties	
1. IUPAC Name	Isobutyltrimethylpentane, 2,2,4-Trimethylpentane
2. Appearance	Colourless liquid
3. Molecular formula	C_8H_{18} or $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
4. Molecular weight	114.22 g/mol
5. Melting point ^0C	-107.38 °C
6. Boiling point ^0C	99.3 °C
7. Density	0.688 g/ml, liquid
8. Specific gravity	0.692

Source: Safety (MSDS) for 2,2,4-trimethylpentane

2.3 RUBBER SEED OIL

The rubber plant is a natural source of rubber that has been reported to have oil rich seeds. There are variations in the oil content of the seed for different countries, the average oil yield have been reported to be 40 %. The oil has found little or no economic importance except for scanty reports on its possible uses in soap, alkyd resin and lubricating oil industries. The vegetable oil has the industrial value that depends on its

specified fatty acids and the ease with which it can be combined or modified with other chemicals. The percentage of saturated fatty acids (myristic, palmitic, stearic, arachidic, and behenic) in rubber seed oil is 17 – 20 % and the composition of unsaturated fatty acids (palmitoleic, oleic, linoleic, linolenic and arachidolic) is 77 – 82 % (Njoku et al., 1996).

Rubber seed oil (RSO) produces the same power output like diesel but with reduced thermal efficiency and increased smoke emission because of the high viscosity of RSO, which leads to sluggish combustion (Edwin Geo V. et al., 2009). The rubber seed oil has viscosity more than 50 cSt. Besides, rubber seed oil is found to be a promising alternative fuel source for compression ignition engines (Ramadhas A.S. et al., 2005). It does not need any major modification in the structure of the engine.

Table 2.2 : Properties of Rubber Seed Oil in Comparison with The Other Oils

Table 1
Properties of rubber seed oil in comparison with the other oils

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

Source: Ramadhas A. S. et al. (2005)

2.4 BIORENEWABLE FUELS FROM VEGETABLE OIL

The term of biofuel or biorenewable fuel (refuel) is referred to as solid, liquid or gaseous fuels that predominantly produced from biomass (Demirbas A, 2009). Production of biofuel requires to grow crops and convert them to biofuels (Hill J et al., 2006). Oxygen content is the biggest difference between petroleum feed stock and

biofuels (Demirbas A, 2009). One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). Biofuel are non-polluting, locally available, sustainable, accesible and reliable fuel obtain from renewable source. Many researches have shown that particulate matter, unburned hydrocarbons, carbon monoxide and sulphur levels are significantly less in the exhaust gas while using biodiesel as fuel (Ramadhas A.S. et al., 2005). After it was known that fossil fuels are finite and indeed will only suffice for a few generations, scientists have been looking for alternative fuels (Klopfenstein and Walker, 1983).

Vegetables oils from biorenewable oil seed can be used when mixed with diesel fuels. The viscosities of vegetable oils are much higher compared with usual diesel fuel and require modifications of the engine if it is used as fuels for diesel engines. Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. When the temperature of oil is increased, its viscosity will decreases and it is therefore able to flow more readily. Viscosity is the most important property of biofuel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. There are several ways to reduce the viscosity of vegetable oils for example microemulsification, dilution, pyrolisis, catalytic cracking and transesterification. Pyrolysis process has more advantages than transesterification because it can produced liquid fuel with similar chemical components to conventional petroleum diesel fuel. Even, vegetable oils can be converted to a maximum of liquid and gaseous hydrocarbons by pyrolisis, decarboxylation, deoxygenation and catalytic cracking processes.

There has been growing interest in biodiesel, it is made from natural, renewable sources for example vegetables fat and oils. Biodiesel whether it in triacylglycerols or trans-esterified with various monohydric alcohols (Klopfenstein and Walker, 1983). Ethanol produced from biomass shows promise as a future fuel for spark ignition (SI) engines because it contains of high octane number of quality. However, ethanol also has disadvantage for example it is not suitable for compression ignition engine (CI) because of its low cetane number (Edwin Geo V. et al., 2009). Vegetable

oils have comparable energy density, cetane number, heat of vaporization and stoichiometric air-fuel ratio with that of the diesel fuel (Ramadhas A.S. et al., 2005).

In the near future, vegetable oils have the potential to replace a fraction of petroleum distillates and petroleum-based petrochemicals. If compared to any other thermochemical process, pyrolysis received a significant amount of interest due to better quality of product. There are more than 350 identified oilbearing crops, among which only sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for diesel engines. Limitations to vegetable oil use are potential production and costs. Moreover, production of vegetable oil is limited by the land area available. Vegetable oil fuels are more expensive than petroleum fuel. Therefore, vegetable oil fuels are not petroleum-competitive fuel. However, due to recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils as a fuel.

2.5 FATTY ACID

Fatty acid is a carboxylic acid with long hydrocarbon chain. The general formula is R-$(CH_2)_n$-COOH. The most usual length of hydrocarbon chain is 12-18 but it may vary from 10-30 carbons. The non-polar hydrocarbon alkane chain is an important counter balance to the polar acid functional group. The acid functional group dominates and gives the whole molecule a polar character in acids. It different for fatty acids, the non-polar hydrocarbon chain gives the molecule a non- polar character. Fatty acid methyl esters originating from vegetable oils and animal fats are known as biodiesel (Miao X. and Wu Q., 2006). The fatty acids contained in rubber seed oil are oleic, linoleic and linolenic acids as unsaturated fatty acids, followed by palmitic and stearic acids as saturated fatty acids. Their structures are as shown in Figure 2.2. All those fatty acids in the oil mainly composed lionleic acid, oleic acid, cetane acid by hydrolysis, gas chromatography analysis and esterification.

Figure 2.1 : Fatty Acid Structure

Source: Ikwuagwu O.E. et al. (2000)

The saturated fatty acids have no double bonds, while oleic acid is an unsaturated fatty acid has one double bond (also described as olefinic) and polyunsaturated fatty acids like linolenic acid contain two or more double bonds. Saturated fatty acids are evenly filled out with hydrogen, which remains solid at room temperature. Poly unsaturated fatty acids remain liquid at room temperature. If it needs to be solidified, it has to be hydrogenated, or saturated with hydrogen by breaking the carbon double bonds and attaching hydrogen.

Lauric acid (also called Dodecanoic acid) is the main acid in coconut oil (45 - 50 percent) and palm kernel oil (45 - 55 percent). Nutmeg butter is rich in myristic acid (also called Tetradecanoic acid) which constitutes 60-75 percent of the fatty-acid content. Palmitic acid (also called Hexadecylic acid) constitutes between 20 and 30 percent of most animal fats and is also an important constituent of most vegetable fats (35 - 45 percent of palm oil). Stearic acid (also called Octadecanoic Acid) is nature's most common long-chain fatty acids, derived from animal and vegetable fats. It is widely used as a lubricant and as an additive in industrial preparations. It is used in the manufacture of metallic stearates, pharmaceuticals, soaps, cosmetics, and food packaging. It is also used as a softener, accelerator activator and dispersing agent in rubbers. Oleic acid (systematic chemical name is cis-octadec-9-enoic acid) is the most abundant of the unsaturated fatty acids in nature.